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Neutron diffraction and Mössbauer studies on $Fe_{1-x}Cr_2S_4(x=0.0, 0.04, 0.08)$

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Polycrystalline samples of $Fe_{1-x}Cr_2S_4(x=0.0, 0.04, 0.08)$ have been studied with x-ray and neutron powder diffraction, Mössbauer spectroscopy, magnetization, and magnetoresitance (MR) measurements. Neutron diffraction patterns were obtained at various temperature ranges from 10 K to room temperature. Neutron diffraction on $FeCr_2S_4$ above 10 K shows that there is no crystallographic distortion and reveals antiferromagnetic ordering, with the magnetic moment of Fe^{+2} ($-3.52\ \mu_B$) aligned antiparallel to Cr^{3+} ($2.72\ \mu_B$). Mössbauer spectra shows asymmetric line broadening in the temperature range from 13 to 170 K and it is considered to be dynamic Jahn–Teller stabilization. The charge states of the iron ions are ferrous in character. With increasing Fe deficiency, the peak of maximum magnetoresistance of $x=0.0$, 0.04, and 0.08, occurred at 171, 174, and 186 K, respectively. The increasing temperature of the MR peak position is interpreted as due to an enhancement of activation energy.
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I. INTRODUCTION

Recently the colossal magnetoresistance effects in sulphur spinel compounds ($Fe_{1-x}Cu_xCr_2S_4$; $x=0$, 0.5) have been reported, and it is suggested that the conduction mechanism in these materials may not be the double exchange of carriers.[1] Since the crystal and magnetic structures are different from Mn perovskites, renewed interest has been focused on the conduction mechanism of sulphur spinel compounds. Yang *et al.*[2] claimed magnetic polaron model in $FeCr_2S_4$ by electron spin resonance study and Greaves and co-worker[3] reported unusual reduction of Fe magnetic moment by neutron diffraction study. Also Min and co-workers[4] interpreted its conduction mechanism by half-metallic properties. Very recently, Kang *et al.*, published a paper on $Cu_{0.5}Fe_{0.5}Cr_2S_4$ by valence band photoemission study and reported monovalence of copper and the ferric character of iron ions.[5] Mössbauer studies on $FeCr_2S_4$ have previously been reported by many workers.[6,7] According to the octahedral (B) site preference of Cr^{3+}, it is believed that the Mössbauer spectra on $FeCr_2S_4$ are composed of the tetrahedral (A) site Fe^{2+} spectra. But the Mössbauer spectra on $FeCr_2S_4$ were found to be dependent on the sample, furthermore some of the paper reported the line broadening originating from the excess of B site Fe^{2+}. These difficulties may be eliminated by starting with a small iron deficiency.[8] Therefore it is essential to determine the valence state and magnetic structure of iron ions in various sulfur spinel compounds to understand the underlying backgrounds properly. Here we present the results of Mössbauer experiments and compare them with those of x-ray, neutron diffraction, magnetoresistance, superconducting quantum interference device (SQUID) magnetometer for sulfur spinel compounds.

II. EXPERIMENT

$Fe_{1-x}Cr_2S_4(x=0.0, 0.04, 0.08)$ were prepared by the direct reaction of the high-purity elements Fe, Cr, Cu, and S in an evacuated quartz tube. The crystal structures of the samples were examined by an x-ray diffractometer with Cu $K\alpha$ radiation and neutron diffractometer at the Korea Atomic Energy Research Institute HANARO HRPD (high resolution powder diffractometer, $\lambda=1.8348$ Å) reactor. The Mössbauer spectra were recorded using a conventional spectrometer of the electromechanical type with a ^{57}Co source in a rhodium matrix.

III. RESULTS AND DISCUSSION

The x-ray (Cu $K\alpha$ radiation) and neutron diffraction patterns for samples exhibited the cubic spinel phase for all our sulfur spinel samples. In order to examine whether there is static Jahn–Teller distortion in $FeCr_2S_4$, we obtained neutron diffraction patterns from 10 to 300 K. Crystal structure is determined to be cubic spinel of $Fd3m$ by Rietveld refinement. Figures 1(a) and 1(b) show the results of neutron diffraction refinement for $FeCr_2S_4$, at 10 and 175 K, respectively. The determined lattice constants, oxygen parameter u, Bragg factor R_b, R_{ex}, and magetic factor R_m, and magnetic moments of atoms are listed in Table I. Figure 1(b) shows the diffraction pattern of paramagnetic nucleus peaks. In Fig. 1(a) we could not find any other different positions of magnetic superstructure peaks other than nucleus peaks. Namely, all magnetic peaks are overlapped on nucleus peaks. Therefore it is concluded that intersublattice superexchage interaction of Fe(A)–Cr(B) is antiferromagnetic, while intrasublattice superexchange interaction of Fe(A)–Fe(A) and Cr(B)–Cr(B) is ferromagnetic, respectively.

Figures 2(a), 2(b), and 2(c) show the temperature dependence of zero-field resistance, resistance measured in the field of 1.6 T, and magnetoresistivity defined as $MR_H(T)$

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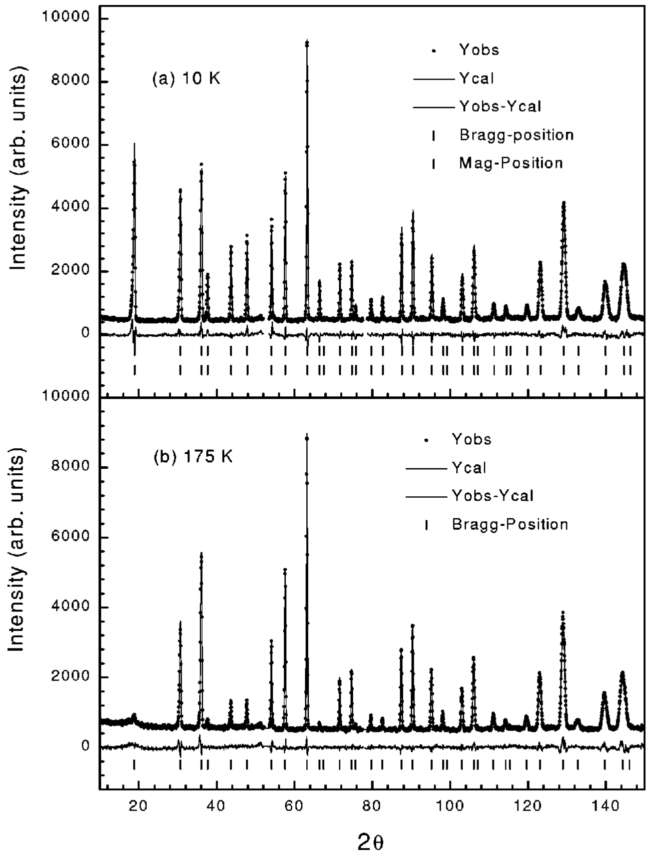

FIG. 1. Refined neutron diffraction patterns of $FeCr_2S_4$ (a) 10 K, (b) 175 K. The closed circle and continuous lines represent the observed, calculated and difference (obsacal) profiles, respectively. Tick marks of the upper and lower panels show the positions of nucleus and magnetic reflections, respectively.

$=[R(0)-R(1.6T)]/R(0)$, which is in agreement with the result reported by Ramirez.[1] It shows metallic behavior in the temperature range between 140 and 170 K, while semiconducting behavior at $T>170$ K and $T<140$ K. Even though $\mathrm{MR}_H(T)$ is lower than that of the Mn perovskite, obvious MR effects are shown.

Figures 3(a), 3(b), and 3(c) show the temperature dependence of SQUID magnetization for the samples $x=0.0$, 0.04, 0.08, respectively. The Néel temperature (T_N), which is defined as the temperature of the maximum slope in dM/dT, is indicated by an arrow on the magnetization curve. The determined Néel temperature (T_N) for the sample $x=0.0$, 0.04, 0.08 were 172, 170, and 169 K, respectively. As shown in Fig. 2, for the sample with $x=0.0$, 0.04, 0.08, magnetoresistance peaks at T_M, 172, 174, 184 K, with the $\mathrm{MR}_H=10\%$, 14%, 12%, respectively. It is noticeable that with increasing Fe deficiency the separation between T_N and T_M grows gradually. Assuming a simple exponential dependence of the form $R(T)=R_0\exp(E_\rho/k_BT)$, a fit to the data of Figs. 2(a), 2(b), and 2(c) above T_M yields activation energy $E_\rho=46$, 52, 58 meV, respectively. This result for $x=0.0$ is in good agreement with the value reported previously.[1] The inset of Figs. 3(a)–3(c) shows the enlarged shape of magnetization between 4 and 20 K. This cusp-like anomaly at 9 K is explained by changing from static to dynamic Jahn–Teller stabilization.[7]

TABLE I. Results of refinement parameters of neutron diffraction on $FeCr_2S_4$ [$Fd3m$;Fe(8a),Cr(16d),S(32e;(u,u,u))].

	10 K	175 K
a/Å	9.9756(3)	9.9813(3)
u (S)	0.3834(3)	0.3843(3)
μ_B (Fe)	−3.52	
μ_B (Cr)	2.72	
R_{exp}	3.76%	3.66%
R_b	4.62%	4.45%
R_m	4.97%	

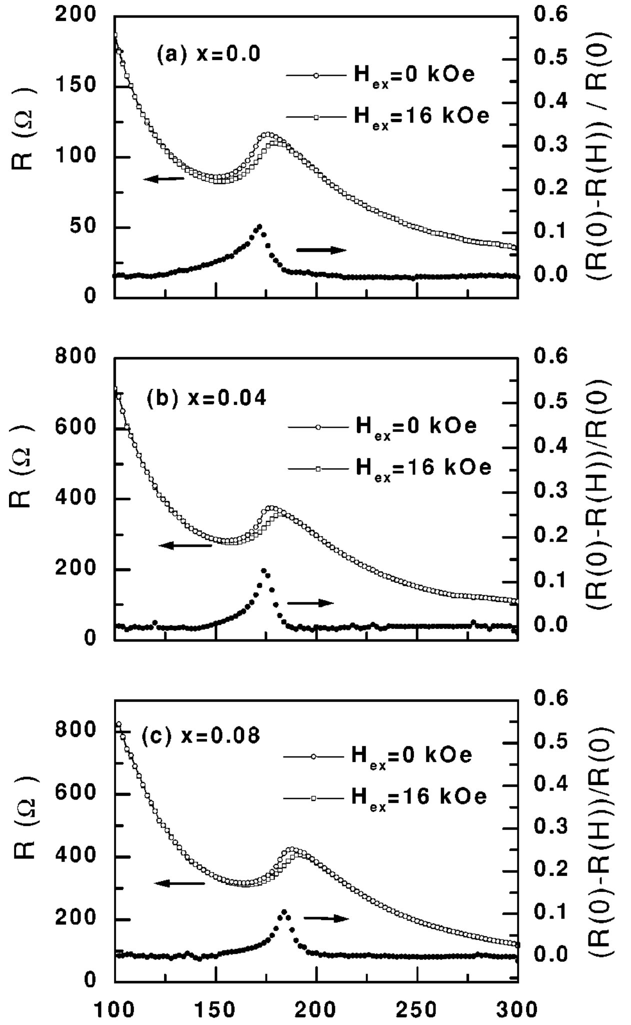

FIG. 2. Temperature dependence of zero field resistance R, resistance measured at 1.6 T, and magnetoresistance MR_H at 1.6 T, where $\mathrm{MR}_H=(R(0)\text{-}R(1.6T))/R(0)$, for (a) $x=0.0$, (b) $x=0.04$, (c) $x=0.08$, respectively.

In order to study the conduction mechanism and local properties of $Fe_{1-x}Cr_2S_4(x=0.0, 0.04, 0.08)$, Mössbauer spectra of the sample were measured at various absorber temperatures from 13 K to room temperature. Some of the representative spectra for the sample $Fe_{0.96}Cr_2S_4(x=0.04)$ are shown in Fig. 4. We analyzed the Mössbauer spectra using–eight Lorentzian fitting methods. The detailed procedures are expressed in Ref. 8. The isomer shift at room temperature is 0.60 mm/s relative to Fe metal, which means that the charge of Fe ions is ferrous in character. In this sample

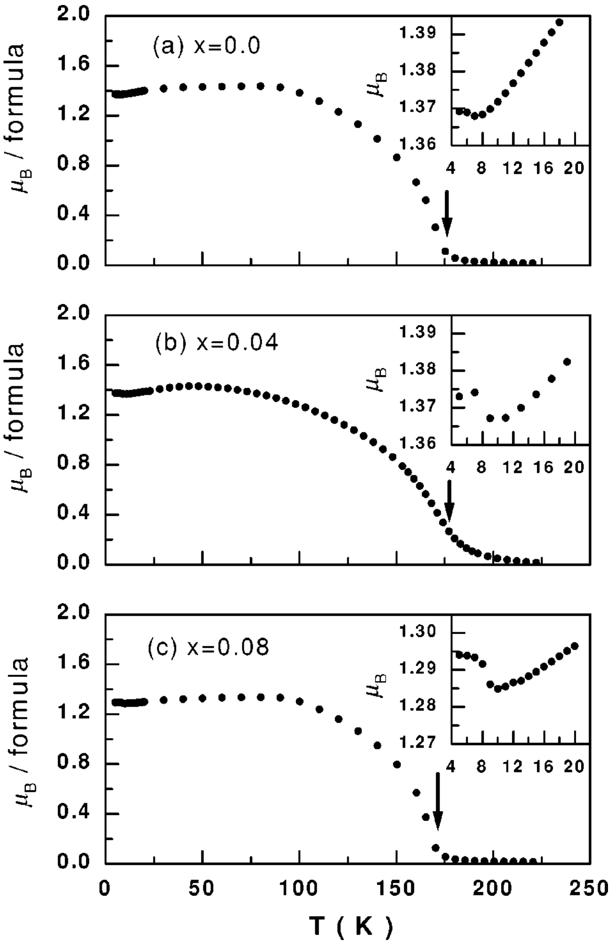

FIG. 3. Temperature dependence of SQUID magnetization M under external field 50 kOe, for (a) $x=0.0$, (b) $x=0.04$, (c) $x=0.08$. The inset shows the enlarged shape of magnetization between the temperatures 5 and 20 K.

magnetic structure is ferrimagnetic and there are no another iron species other than Fe^{2+}. We note that quadrupole splitting E_Q rapidly decreases with increasing temperature. In the tetrahedral site, the ground state of Fe^{2+} is a degenerate orbital doublet ^5E_g.[9] This situation is unstable and must be resolved via a Jahn–Teller distortion, which may explain the observed appearance of quadrupole splitting below T_N. However, low temperature neutron diffraction patterns for $FeCr_2S_4$ in Fig. 1 showed that no static Jahn–Teller distortion appeared down to 77 K.[10,11] Even though no static Jahn–Teller distortion is observed, dynamic Jahn–Teller distortion can cause a quadrupole shift if the distortion relaxes between a number of equivalent crystal axes.[12,13] This kind of relaxation consists of the asymmetrical line broadening apparent in Fig. 4. We also note that an unusual increase is observed in H_{hf} below 80 K as temperature increased. The unusual increase of the magnetic hyperfine field below 80 K may be explained in terms of a cancellation effect between the mutually opposite H_L and H_C.[14,15] Here H_L and H_C are the orbital current field and the Fermi-contact field, respectively.

In summary, we have studied magnetic properties and the conduction mechanism in $Fe_{1-x}Cr_2S_4(x=0.0, 0.04, 0.08)$. With increasing Fe deficiency the maximum magnetoresistance temperature increased steadily. The Mössbauer spectra result is explained in terms of dynamic Jahn–Teller effect.

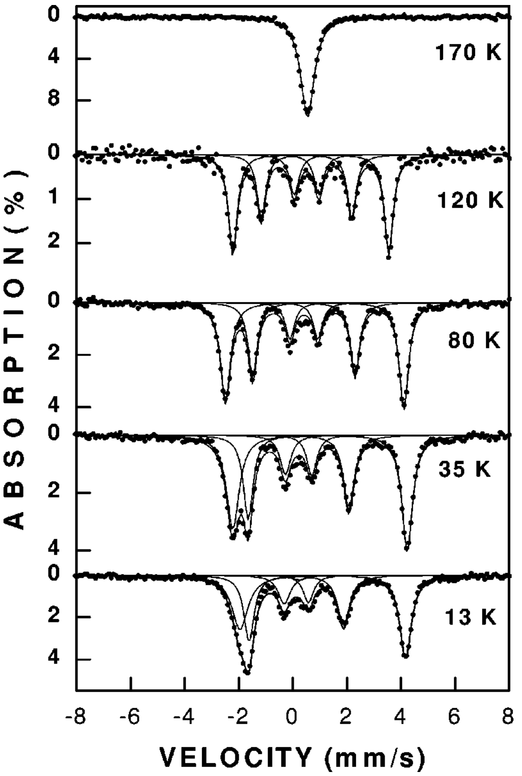

FIG. 4. Mössbauer spectra of the $Fe_{0.96}Cr_2S_4(x=0.04)$ at various temperatures.

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